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# Characterisation of covalent copper and manganese organometallic complexes with Schiff bases by ionspray mass spectrometry

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**Abstract**

Copper and manganese complexes containing Schiff bases as ligands, having potential interest in homogeneous catalysis, have been characterised by mass spectrometry using ionspray ionisation. Single stage mass spectrometry allowed us to confirm the molecular weight of complexes in all cases, providing also interesting information about the real form present in solution. Complete structural characterisation of the complexes has been obtained by tandem mass spectrometry, by the analysis of the fragments formed after collisionally induced dissociation of selected precursor ions inside the collision cell of a triple quadrupole mass spectrometer. 

*Keywords:* Ionspray mass spectrometry; Manganese complexes; Schiff base complexes

## 1. Introduction

Transition-metal complexes constitute one of the most representative class of catalysts in modern catalytic reactions [1], including natural enzymatic systems [2]. In recent years, the use of manganese and copper complexes as catalysts has received a great deal of attention. In particular, Mn(III)–salen [3] and Mn(III)–porphyrin [4] complexes proved to be excellent catalysts in the epoxidation reaction of olefinic substrates, even for enantioselective catalysis [5]. In addition, a large number of mono- and dinuclear copper complexes have been efficiently used in several catalytic reactions [6]. Some chiral copper complexes proved to be good catalysts in several asymmetric catalytic reactions, such as Baeyer–Villiger oxidation of ketones [7], allylic oxidation reaction [8], aziridination [9] and cyclopropanation [10] of olefins, Michael condensation [11], Diels–Alder and aldol reactions [12].

We were interested in the synthesis of new covalent complexes of copper and manganese with Schiff bases for investigating their catalytic properties and in this frame we prepared the compounds reported in Scheme 1. Structural characterisation of these compounds sometimes is not a trivial task, as they are paramagnetic so that NMR investigation is not immediate. Moreover, the formation of monocrystals suitable for X-ray diffraction analysis is not easy.

Mass spectrometry can be very useful in this respect, as it can provide directly and very rapidly the molecular weight of the complex as well as some structural information by the interpretation of the fragmentation pattern. In principle, traditional electron ionisation (EI) mass spectrometry could be suitable for the study of covalent organometallic complexes, as often they are volatile and stable enough for this ionisation technique. Unfortunately the complexes studied in the present investigation did not provide any result under EI conditions and different mass spectrometric approaches were then necessary. Desorption chemical ionisation (DCI) mass spectrometry has been successfully used for the investigation of similar complexes [11], but we feel that ESI or ionspray (pneumatic-assisted electrospray, ISI) mass spectrometry provides better results. ESI-MS (as well as ISI-MS) is a powerful analytical technique particularly suitable for polar compounds [13]. This technique is widely used nowadays for peptide and protein characterisation and biopharmaceutical analysis [14], whereas its applications in the field of organometallic compounds is quite limited [15], dealing mainly with ionic organometallic compounds [16]. Recently, we began to use ISI-MS for the study of covalent organometallic complexes obtaining very interesting results [17]. This investigation pointed out [18] that covalent

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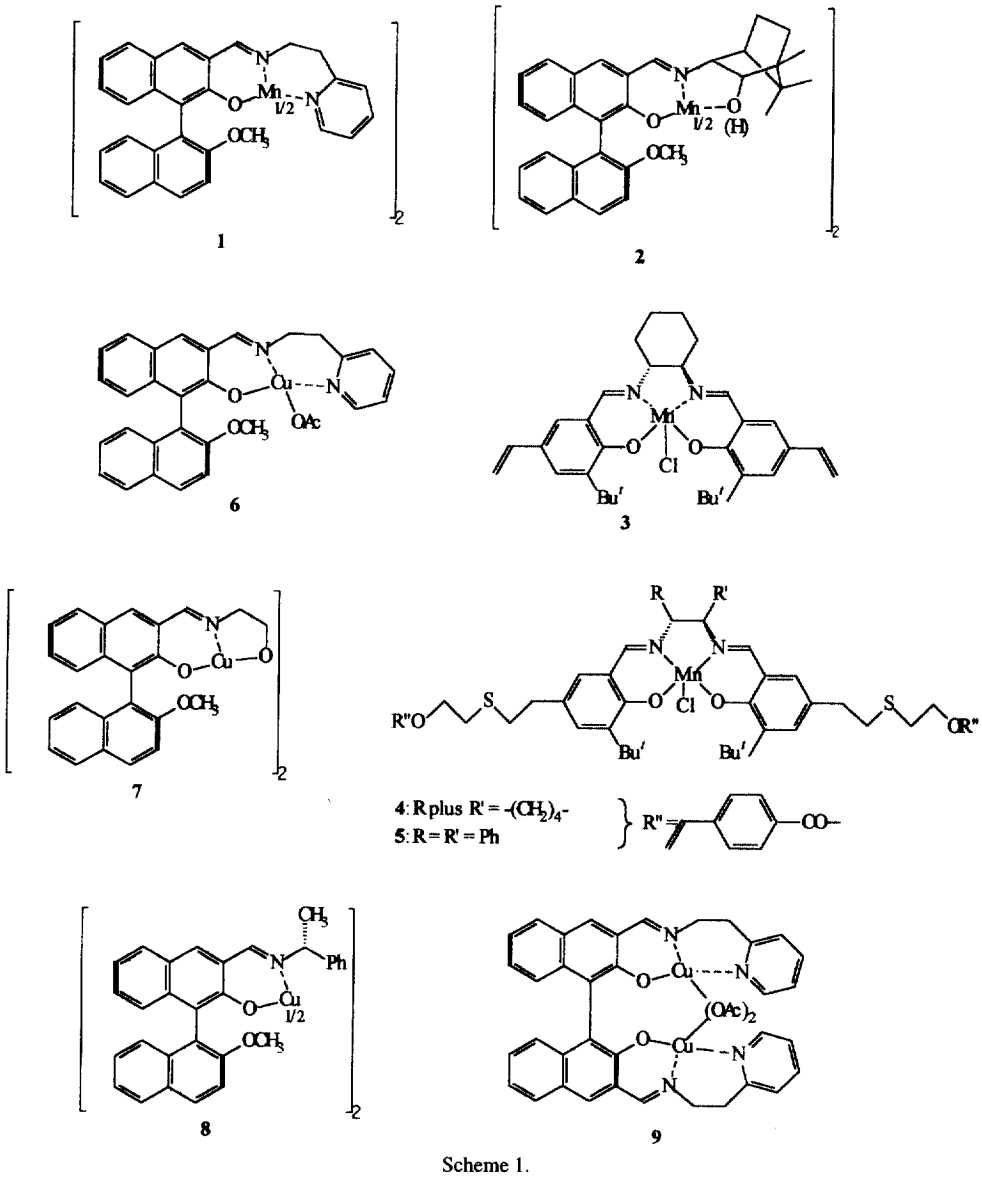



Scheme 1.

organometallic compounds can be analysed by the use of this technique:

1. if there are some possible basic (for positive ions) or acidic (for negative ions) sites in their structure;
2. if there are some sites capable of releasing or accepting one or more electrons, so that redox phenomena can occur;
3. if they have affinity for small cations normally present in solution, such as ammonium, sodium or potassium ions;
4. if some strong electron-withdrawing ligand is present, capable of inducing a $M^+X^-$ polarisation.

As all the complexes examined in the present study have one or more of these features, we decided to check the possibility of using ISI-MS for their characterisation. As is well known, ESI/ISI-MS usually provides molecular weight information, but practically no structural information, since the fragmentation is absent or very low. Tandem mass spectrometry can supply the lacking structural information by measuring product ion spectra of selected precursor ions after collisionally induced dissociation (CID) in the collision cell of a triple quadrupole mass spectrometer.

## 2. Experimental

### 2.1. General remarks

Melting points (uncorrected) were measured with a Kofler hot-stage apparatus. Optical rotations were measured on a JASCO Dip 360 (Jasco, Tokyo, Japan) automatic polarimeter. $^1$H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz, Varian, Palo Alto, CA, USA). Chemical shifts are denoted in $\delta$-units (ppm) relative to tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard or relative to residual solvent peaks ($CHCl_3$, $\delta = 7.26$ ppm). The splitting patterns are indicated as follows: s (singlet), d (doublet), dd (double doublet), ddd (double double dou-

blet), triplet (t), q (quartet), m (multiplet) and br (broad). $^{13}C$ NMR spectra were recorded on the same spectrometer (50.3 MHz). Chemical shifts ($\delta$, ppm) are relative to the solvent and are converted to the TMS scale using $\delta(CHCl_3) = 76.91$ ppm. Splitting patterns for $^{13}C$ NMR spectra, determined with the APT pulse sequence, are indicated as follows: s (singlet; quaternary C), d (doublet, –CH=), t (triplet, $-CH_2-$), q (quartet, $-CH_3$). Electron ionisation mass spectra (EI-MS) and high resolution mass spectrometry (HRMS) for accurate mass determination were obtained using a VG 70-70E double-focusing (EB) mass spectrometer (Fisons Instruments, VG Analytical, Manchester, UK) equipped with a DEC PDP-11/23 computer (Digital Equipment Corporation, Maynard, MA, USA). Low-resolution EI spectra were obtained under the following conditions: ionizing energy, 70 eV; emission current, 1.0 mA; source temperature, 200°C; scan range, *m/z* 30–600; scan rate, 1 s/decade, interscan delay, 0.5 s; resolution, 1000 (10% valley definition). Sample introduction was via a heated (300–350°C) direct insertion probe. For accurate mass determinations, obtained via Data System after a multichannel acquisition (MCA) of 10 scans summed, the resolution was adjusted to 5000; the scan rate, 10 s/decade; calibrant for accurate mass, perfluorokerosene (PFK) introduced through the septum inlet.

Elemental analyses were performed in Istituto di Chimica Farmaceutica e Tossicologica, Università di Pisa, by Mr Pascelli, or in the Microanalytical Department of the University of Groningen (Netherlands), by Messrs H. Draaijer, J. Ebels and J. Hommes. Analytical TLC was performed on 0.2 mm silica gel plate Merck 60 F-254 (Merck, Darmstadt, Germany) and flash chromatography [19] was carried out with silica gel Merck 60 (230–400 mesh). 2-(2′-Pyridyl)-ethylamine, 2-aminoethanol, 2-aminophenol and (+)-(*R*)-1-phenylethylamine were purchased by Aldrich Chimica (Aldrich, Milwaukee, WI, USA). The following compounds were synthesised using literature procedures: (*S*)-(−)-2-hydroxy-2′-methoxy-1,1′-binaphtyl-3-carboxaldehyde (**10**) [20]; *cis–exo*-3-aminoisoborneol (**11**) [21]; (*S*)-(−)-2,2′-dihydroxy-1,1′-binaphtyl-3,3′-dicarboxaldehyde (**12**) [22]. The synthetic procedures as well as characterisation data of the following compounds have already been published [23]: [(*R,R*)-*N,N′*-bis(3-tert-butyl-5-vinylsalicylidene)-1,2-cyclohexanediaminato(2-)]manganese(III) chloride (**3**); {(*R,R*)-*N,N′*-bis{3-tert-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-cyclohexanediaminato(2-)}manganese(III) chloride (**4**); {(*R,R*)-*N,N′*-bis{3-tert-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-diphenyl-1,2-ethanediaminato(2-)}manganese(III) chloride (**5**).

### 2.2. Ionspray mass spectrometry

Ionspray mass spectra were performed on a Perkin-Elmer Sciex API III plus triple quadrupole mass spectrometer (Sciex Co., Thornhill, Ont., Canada) equipped with an API ion source and an articulated ionspray interface. The spectra were obtained under the following experimental conditions: ionspray voltage, 5.5 kV; orifice voltage, 60 V; resolution above 1 Da; scan range and scan rate, as appropriate depending on the sample. The samples were dissolved in methanol (about 10 μM) and the resulting solution was delivered to the mass spectrometer by continuous infusion by a syringe pump (Harvard model 22, Harvard Apparatus, Inc., South Natick, MA, USA) at 5 ml/min or by flow injection analysis (FIA) using a Perkin-Elmer series 200 dual solvent HPLC pump (Perkin-Elmer Co., Norwalk, CT, USA) equipped with a 7125 Rheodyne injector with a 20 ml loop (Rheodyne Inc., Cotati, CT, USA) using 1:1 $MeOH/H_2O$ as a mobile phase, flowing at 50 ml/min.

### 2.3. Product ion analysis

ISI product ions were produced by collisionally induced dissociation (CID) of selected precursor ions in the collision cell of the PE Sciex API III plus instrument and mass-analysed using the second analyser of the instrument under the same experimental conditions described above for the ISI spectra. Other experimental conditions for CID included: collision energy, 20–40 eV depending on the sample; collision gas, Ar; collision gas thickness (CGT), $230 \times 10^{13}$ molecules/cm$^2$ (CGT is an indication of the collision conditions: it corresponds to the collision gas pressure inside the collision cell times the length of the collision cell itself); scan range, as appropriate depending on the sample.

### 2.4. Reactions and characterisation data

#### 2.4.1. (−)-2′-Methoxy-3-{[2-(2-pyridyl)ethylimino]-methyl}-(S)-[1,1′]-binaphthalene-2-ol (13)

To a solution of 300 mg (0.914 mmol) of **10** in hot absolute ethanol (25 ml) were added 112 mg (0.914 mmol) of 2-(2′-pyridyl)-ethylamine in the same solvent (5 ml), and the mixture was stirred under a very gentle reflux for 1 h. After cooling down, a yellow needle crystalline solid precipitated, it was collected by filtration and washed with small portions of cold ethanol and dried under vacuum, to give 305 mg (77% yield) of pure Schiff base **13**: m.p. 186°C; $[\alpha]_D^{25} = -201$ (*c* 0.497, $CH_2Cl_2$); $^1H$ NMR $\delta$ 3.14 (t, $J = 7.1$ Hz, 2H), 3.77 (s, 3H), 4.05 (t, $J = 7.1$ Hz, 2H), 7.07–7.19 (m, 3H), 7.21–7.38 (m, 5H), 7.46 (d, $J = 8.9$ Hz, 1H), 7.51 (dt, $J = 1.9$, 7.7 Hz, 1H), 7.81–7.87 (m, 3H), 7.97 (d, $J = 9.0$ Hz, 1H), 8.52–8.53 (m, 1H), 8.54 (s, 1H), 13.03 (s, 1H); $^{13}C$ NMR $\delta$ 39.23 (t), 56.98 (q), 59.38 (t), 114.29 (d), 117.17 (s), 118.94 (s), 120.79 (s), 121.48 (d), 123.13 (d), 123.54 (d), 123.68 (d), 124.83 (d), 125.12 (d), 126.40 (d), 127.29 (s), 128.02 (d, 2C overlapped), 128.65 (d), 129.38 (s), 129.63 (d), 132.96 (d), 133.80 (s), 135.32 (s), 136.37 (d), 149.41 (d), 154.54 (s), 155.09 (s), 158.99 (s), 165.54 (d); MS (EI) *m/z*: 432 ($M^{\cdot+}$, 100), 401 (74), 289 (58), 107 (94), 106 (77); HRMS *m/z* Calc. for $C_{29}H_{24}N_2O_2$: 432.184. Found: 432.184.

*2.4.2. (−)-3-[(cis–exo-Isoborneolyl-3-imino)methyl]-2'-methoxy-(S)-[1,1']-binaphthalene-2-ol (14)*

To a solution of 250 mg (0.761 mmol) of **10** in hot absolute ethanol (20 ml) was added 129 mg (0.762 mmol) of **11**. Then the same procedure as for **13** was followed. After cooling down, the reaction mixture was concentrated to half volume and left overnight. A yellow needle crystalline solid precipitated. It was collected, washed with a small portion of cold ethanol and dried under vacuum (268 mg, 0.558 mmol, 73%), to give **14**: m.p. 225°C; $[\alpha]_D^{25} = -90.8$ (*c* 0.566, $CH_2Cl_2$); $^1$H NMR $\delta$ 0.83 (s, 3H), 0.99 (s, 3H), 1.15 (s, 3H), 1.19–1.28 (m, 2H), 1.59–1.92 (m, 4H), 3.67 (d, $J$ = 7.6 Hz, 1H), 3.80 (s, 3H), 3.84 (d, $J$ = 7.4 Hz, 1H), 7.07–7.12 (m, 1H), 7.22–7.38 (m, 5H), 7.49 (d, $J$ = 9.0 Hz, 1H), 7.87–7.91 (m, 2H), 7.96 (s, 1H), 8.00 (d, $J$ = 9.0 Hz, 1H), 8.67 (s, 1H), 12.38 (s, 1H); $^{13}$C NMR $\delta$ 11.33 (q), 21.58 (q), 21.77 (q), 26.53 (t), 33.54 (t), 47.31 (s), 49.26 (s), 53.02 (d), 56.93 (q), 77.19 (d), 81.91 (d), 114.28 (d), 117.20 (s), 118.76 (s), 121.11 (s), 123.22 (d), 123.49 (d), 124.91 (d), 125.28 (d), 126.33 (d), 127.20 (s), 128.02 (d), 128.17 (d), 128.72 (d), 129.32 (s), 129.67 (d), 133.60 (d), 133.87 (s), 135.56 (s), 154.29 (s), 155.32 (s), 166.54 (d); MS (EI) *m/z*: 479 ($M^{\cdot+}$, 100), 448 (55), 364 (26), 336 (53), 327 (94), 313 (38), 298 (32), 281 (26), 239 (32), 183 (45); HRMS *m/z* Calc. for $C_{32}H_{33}NO_3$: 479.246. Found: 479.245.

*2.4.3. (−)-Bis{2'-methoxy-3-{[2-(2-pyridyl)ethylimino]-methyl}-(S)-[1,1']-binaphthalene-2-olato}manganese(III) chloride (1)*

To a solution of the ligand **13** (437 mg, 1.01 mmol) in hot ethanol (10 ml) was added a solution of $Mn(OAc)_2 \cdot 4H_2O$ (495 mg, 2.02 mmol) in ethanol (5 ml), and the resulting mixture was heated under reflux for 1 h. After addition of 127 mg of LiCl (3.01 mmol) to the mixture, it was refluxed for additional 30 min. The solvent was then evaporated under vacuum and the residue was dissolved in $CH_2Cl_2$. The organic phase was washed with water, and dried over $Na_2SO_4$. Evaporation of the solvent afforded the complex **1** as a dark brown solid (808 mg, 84% yield from **13**): m.p. 153 − 155°C. Ionspray MS *m/z* 917 $[M–Cl]^+$; ionspray MS-MS *m/z* 917 (97), 812 (100), 486 (99). *Anal.* Calc. for $C_{58}H_{46}N_4O_4MnCl$: C, 73.07; H, 4.86; N, 5.88; Cl, 3.72. Found: C, 72.96; H, 4.84; N, 5.74; Cl, 3.27%.

*2.4.4. (−)-Bis{3-[(cis–exo-isoborneolyl-3-imino)methyl]-2'-methoxy-(S)-[1,1']-binaphthalene-2-olato}-manganese(III) (2)*

To a solution of the ligand **14** (537 mg, 1.12 mmol) in hot ethanol (10 ml) was added a solution of $Mn(OAc)_2 \cdot 4H_2O$ (539 mg, 2.20 mmol) in ethanol (5 ml), and the resulting mixture was heated under reflux for 1 h. The solvent was then evaporated under vacuum and the residue was dissolved in $CH_2Cl_2$. The organic phase was washed with water, and dried over $Na_2SO_4$. Evaporation of the solvent afforded the complex **2** as a dark brown solid (1006 mg, 89% yield from **14**): m.p. 194–195°C. Ionspray MS *m/z* 1011 $[M+H]^+$; ionspray MS-MS *m/z* 1011 (100), 845 (36), 515 (27), 480 (54). *Anal.* Calc. for $C_{64}H_{63}N_2O_6Mn$: C, 76.02; H, 6.28; N, 2.77. Found: C, 75.88; H, 6.21; N, 2.69%.

*2.4.5. 2'-Methoxy-3-[(1S)-(1-phenylethylimino)methyl]-(R)-[1,1']-binaphthalene-2-ol (15)*

To a solution of 252 mg (0.767 mmol) of (*S*)-(−)-2-hydroxy-2'-methoxy-1,1'-binaphthyl-3-carboxaldehyde (**10**) in hot absolute ethanol (25 ml) were added 93 mg (0.77 mmol) of (+)-(*R*)-1-phenylethylamine in the same solvent (10 ml), and the mixture was stirred under a very gentle reflux for 2 h. After cooling down, a tiny crystalline yellow solid precipitated. It was collected by filtration and washed with small portions of cold ethanol and dried under vacuum, to give 301 mg (91% yield) of pure ligand **15**: m.p. 265°C; $[\alpha]_D^{25} = -274$ (*c* 0.104, $CH_2Cl_2$); $^1$H NMR: $\delta$ 1.64 (d, $J$ = 6.6 Hz, 3H), 3.69 (s, 3H), 4.63 (q, $J$ = 6.8 Hz, 1H), 7.0–7.1 (m, 1H), 7.1–7.3 (m, 10H), 7.50 (d, $J$ = 9.0 Hz, 1H), 7.85–7.90 (m, 2H), 7.95 (s, 1H), 8.02 (d, $J$ = 9.0 Hz, 1H), 8.69 (s, 1H), 13.13 (s, 1H); $^{13}$C NMR: $\delta$ 24.89 (q), 56.87 (d), 69.11 (q), 114.21 (d), 117.26 (s), 118.82 (s), 120.97 (s), 123.16 (d), 123.55 (d), 124.84 (d), 125.10 (d), 126.46 (d), 126.65 (d), 127.30 (d), 127.41 (s), 128.05 (d), 128.64 (d), 129.35 (s), 129.67 (d), 133.19 (d), 133.79 (s), 135.44 (s), 143.54 (s), 154.48 (s), 155.07 (s), 163.56 (d); MS (EI) *m/z*: 431 ($M^{\cdot+}$, 76), 400 (16), 326 (24), 296 (53), 184 (40), 105 (100); HRMS *m/z* Calc. for $C_{30}H_{25}NO_2$: 431.189. Found: 431.189.

*2.4.6. {2'-Methoxy-3-{[2-(2-pyridyl)ethylimino]methyl}-(S)-[1,1']-binaphthalene-2-olato}-copper(II) acetate (6)*

To a solution of $Cu(OAc)_2 \cdot H_2O$ (92 mg, 0.46 mmol) in ethanol (30 ml) were added 198 mg (0.46 mmol) of ligand **13** in small portions. The mixture was stirred at 50°C for 6 h. After cooling to r.t., the solvent was removed and the dark brown solid residue was recrystallised from n-hexane/$CHCl_3$ yielding complex **6** as dark green needles (221 mg, 87% yield): m.p. 167–169°C (dec.). Ionspray MS *m/z* 494 $[M–AcO]^+$. *Anal.* Calc. for $C_{31}H_{26}N_2O_4Cu$: C, 67.20; H, 4.73; N, 5.06. Found: C, 67.13; H, 4.78; N, 5.00%.

*2.4.7. (−)-3-[(2-Hydroxyethylimino)methyl]-2'-methoxy-(S)-[1,1']-binaphthalene-2-ol (16)*

217 mg (0.661 mmol) of **10** were treated with 40 mg (0.66 mmol) of 2-aminoethanol in ethanol, following the same procedure described for the preparation of ligand **13**, affording 194 mg (79% yield) of **16**: m.p. 267–268°C; $[\alpha]_D^{25} = -68$ (*c* 0.056, $CH_2Cl_2$); $^1$H NMR $\delta$ 3.75–3.78 (m, 2H), 3.80 (s, 3H), 3.85–3.91 (m, 2H), 7.16–7.35 (m, 6H), 7.49 (d, $J$ = 9.0 Hz), 7.87–8.03 (m, 4H), 8.66 (s, 1H); $^{13}$C NMR $\delta$ 56.90 (q), 62.03 (t), 114.12 (d), 117.02 (s), 118.69 (s), 120.69 (s), 123.75 (d), 123.57 (d), 124.87 (d), 125.00 (d), 126.50 (d), 127.38 (s), 128.06 (d), 128.20 (d), 128.75 (d), 129.42 (s), 129.70 (d), 133.26 (d), 133.88 (s), 135.73

(s), 154.16 (s), 155,04 (s), 167.09 (d); HRMS *m/z* ($M^{\cdot+}$) Calc. for $C_{24}H_{21}NO_3$: 371.152. Found: 371.152.

*2.4.8. {3-[(2-Hydroxyethylimino)methyl]-2'-methoxy-(S)-[1,1']-binaphthalene-2-olato}2-[copper(II)]$_2$ (7)*

To a solution of $Cu(OAc)_2 \cdot H_2O$ (54 mg, 0.27 mmol) in ethanol (30 ml) were added 101 mg (0.27 mmol) of ligand **16**. The mixture was stirred at 65°C for 4 h. After cooling to r.t., the solvent was removed and the solid residue was recrystallised from $Et_2O/CHCl_3$ yielding complex **7** as green crystals (88 mg, 74% yield): m.p. 290–300°C (dec.). Ionspray MS *m/z* 865 $[M+H]^+$, dimeric form). *Anal.* Calc. for $(C_{24}H_{19}NO_3Cu)_2$: C, 66.58; H, 4.42; N, 3.24. Found: C, 66.14; H, 4.66; N, 3.15% [1].

*2.4.9. {2'-Methoxy-3-[(1S)-(1-phenylethylimino)methyl]-(R)-[1,1']-binaphthalene-2-olato}2-copper(II) (8)*

Ligand **15** (150 mg, 0.348 mmol) in ethanol (15 ml) was treated with a solution of $Cu(OAc)_2 \cdot H_2O$ (35 mg, 0.17 mmol) in ethanol (15 ml) and the resulting green solution was stirred at 50°C for 15 h. After cooling to r.t., the solvent was removed under vacuum and the residue was recrystallised from n-hexane/$CHCl_3$, yielding complex **8** as tiny green crystals (130 mg, 83% yield): m.p. 269°C. Ionspray MS *m/z* 924 $[M+H]^+$. *Anal.* Calc. for $C_{60}H_{48}N_2O_4Cu$: C, 77.94; H, 5.23; N, 3.03. Found: C, 77.72; H, 4.87; N, 2.98%.

*2.4.10. (−)-3,3'-Bis{[2-(2-pyridyl)ethylimino]methyl}-2,2'-dihydroxy-(S)-[1,1']-binaphthalene (17)*

To a solution of 300 mg (0.876 mmol) of **12** in hot absolute ethanol (20 ml) were added 214 mg (1.75 mmol) of 2-(2'-pyridyl)ethylamine in the same solvent (8 ml). Then the same procedure described for **13** was followed. After slow cooling down, an orange cubic crystalline solid precipitated. It was collected, washed with small portions of cold ethanol and dried under vacuum (298 mg, 62% yield). A further amount (111 mg, 23% yield) of crystalline product could be recovered by partial concentration of the mother liquor. Both the fractions revealed to be pure **17**: m.p. 86.9–87.1°C; $[\alpha]_D^{25} = -87.6$ (*c* 0.591, $CH_2Cl_2$); $^1H$ NMR $\delta$ 3.16 (t, $J=7.1$ Hz, 4H), 4.06 (t, $J=7.1$ Hz, 4H), 7.08–7.31 (m, 10H), 7.53 (dt, $J=7.7$, 1.8 Hz, 2H), 7.85 (m, 2H), 7.89 (s, 2H), 8.54 (m, 2H), 8.56 (s, 2H), 13.18 (s, 2H); $^{13}C$ NMR $\delta$ 39.19 (t), 59.34 (t), 116.53 (s), 120.88 (s), 121.48 (d), 123.26 (d), 123.70 (d), 124.75 (d), 127.48 (s), 128.21 (d), 133.22 (d), 135.19 (s), 136.43 (d), 149.37 (d), 154.67 (s), 158.96 (s), 165.56 (d). Ionspray MS *m/z* 551 $[M+H]^+$; HRMS *m/z* ($M^{\cdot+}$) Calc. for $C_{36}H_{30}N_4O_2$: 550.237. Found: 550.236.

*2.4.11. {3,3'-Bis{[2-(2-pyridyl)ethylimino]methyl}-(S)-[1,1']-binaphthalene-2,2'-diolato}-[copper(II)]$_2$ diacetate (9)*

To a solution of $Cu(OAc)_2 \cdot H_2O$ (92 mg, 0.46 mmol) in ethanol (30 ml) were added 127 mg (0.23 mmol) of ligand **17**. The mixture was stirred at 50°C for 6 h. After cooling to r.t., the solvent was removed under vacuum and the solid residue was recrystallised from ethanol yielding complex **9** as a green powder (160 mg, 88% yield): m.p. 255–260°C. Ionspray MS *m/z* 733 $[M-AcO]^+$. *Anal.* Calc. for $C_{40}H_{34}N_4O_6Cu_2$: C, 60.52; H, 4.32; N, 7.06. Found: C, 61.03; H, 4.48; N, 6.62% [1].

[1] Better analysis results could not be obtained for this compound.

## 3. Results and discussion

All the complexes examined provided nice quality ionspray mass spectra. A typical ISI-MS spectrum of a Mn complex is shown in Fig. 1, whereas the ISI-MS and ISI-MS-MS data for all the samples are summarised in Table 1. The molecular weight of the complex has been confirmed in all cases, and MS-MS granted the structural information necessary for the complete characterisation of the compounds examined.

The ionisation of these compounds occurs in different ways depending on their structure. Manganese complexes with tetradentate (salen-like) ligands (**3**, **4** and **5**) tend to give a heterolytic breakage of the M–X bond. The Mn–Cl bond present in these complexes is indeed quite polarised and, under ISI conditions, it breaks affording the complexed metal cation by loss of a chloride anion. In the case of manganese complexes with tridentate ligands, both of the O–N–N (**1**) and O–N–O (**2**) type, the expected $L_3MnX_2$ (X = Cl or OAc) structure was never observed, finding in all cases a cationic $[(L_3)_2Mn]^+X^-$ complex, in which the manganese atom results fully coordinated by the two ligand molecules, probably in a pseudo-octahedral geometry, as indicated in Scheme 2. In the case of the cation of the complex containing an O–N–O ligand (**2**), one hydroxy group is deprotonated and the oxygen atom is s-bonded to the Mn atom, whereas the other hydroxyl group maintains its proton and is only coordinated to the metal, that is always in the III oxidation state.

As far as copper complexes are concerned, we investigated the complexation with tridentate ligands (of the type O–N–N and O–N–O), a bidentate ligand (O–N) and a dinucleating

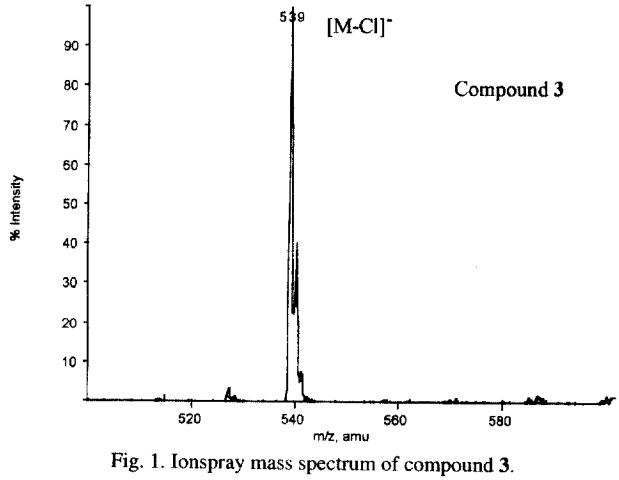
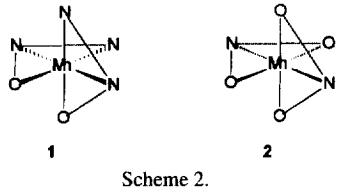



Fig. 1. Ionspray mass spectrum of compound **3**.

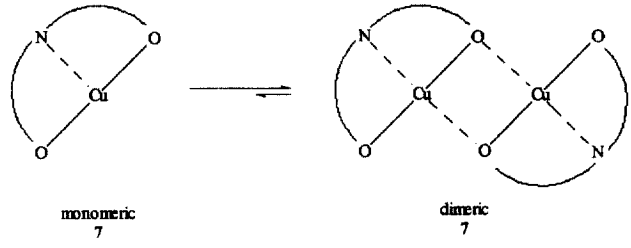
Table 1
ISI-MS and ISI-MS-MS data of the Cu and Mn complexes examined

| Entry | Complex | ISI-MS | | ISI-MS-MS |
|---|---|---|---|---|
| | | *m/z* | Ion | *m/z* (%) |
| 1 | **1** | 917 | $(M-Cl)^+$ | 917 (97), 812 (100), 486 (99) |
| 2 | **2** | 1011 | $(M+H)^+$ | 1011 (100), 845 (36), 512 (27), 480 (54) |
| 3 | **3** | 539 | $(M-Cl)^+$ | 539 (55), 524 (100), 508 (22), 468 (30) |
| 4 | **4** | 955 | $(M-Cl)^+$ | 955 (28), 586 (19), 558 (49), 538 (52), 526 (100), 485 (69) |
| 5 | **5** | 1053 | $(M-Cl)^+$ | 1053 (100), 752 (10), 624 (22), 469 (17) |
| 6 | **6** | 494 | $(M-AcO)^+$ | 494 (43), 464 (100), 437 (7), 375 (12), 357 (4), 183 (10) |
| 7 | **7** | 865 | $(M+H)^+$ | 865 (3), 512 (2), 494 (80), 463 (100), 433 (9), 183 (10) |
| 8 | **8** | 924 | $(M+H)^+$ | 924 (93), 819 (9), 532 (13), 494 (59), 463 (100) |
| 9 | **9** | 733 | $(M-AcO)^+$ | 733 (3), 673 (100), 646 (2), 568 (2), 490 (1) |
| | | 337 | $(M-2AcO)^{2+}$ | 479 (50), 448 (35), 337 (21), 195 (93), 168 (59), 106 (100) |

ligand. The data obtained with copper complexes are somewhat even more interesting than those obtained with Mn complexes. The Cu complex with an O–N–N tridentate ligand (**6**) behaves the same as the Mn complexes with tetradentate ligands, and we observed the $[M-acetate]^+$ ion. Fig. 2 shows a typical spectrum of a copper complex and the comparison with the theoretical isotopic pattern, found in a very good agreement with the experimental data. In this case the complex is monomeric because it contains a monocharged ligand, and an additional one-electron ligand is necessary to neutralise the second positive charge of the copper(II). In this way the metal is fully coordinated (four atom donors) probably in a pseudo-tetrahedral fashion. In the case of O–N–O ligands, as for complex **7**, it contains a double charged ligand, so that there is no need of an additional one-electron ligand, as the two positive charges of the metal are completely neutralised by the ligand itself. In a monomeric form, the copper is coordinatively unsaturated, as it has got only three coordinating donor atoms (Scheme 3). Therefore, one of the four available sites for coordination would be empty in a monomeric structure and would become quite unstable and eager to get the fourth coordinating atom donor. In the dimeric form shown in Scheme 3, both the copper atoms are tetracoordinated with the three atom donors of their own ligand, and with the lone pair of the oxygen atom (probably the alcoholic oxygen) of the other ligand molecule. In this way,




Scheme 2.




Scheme 3.

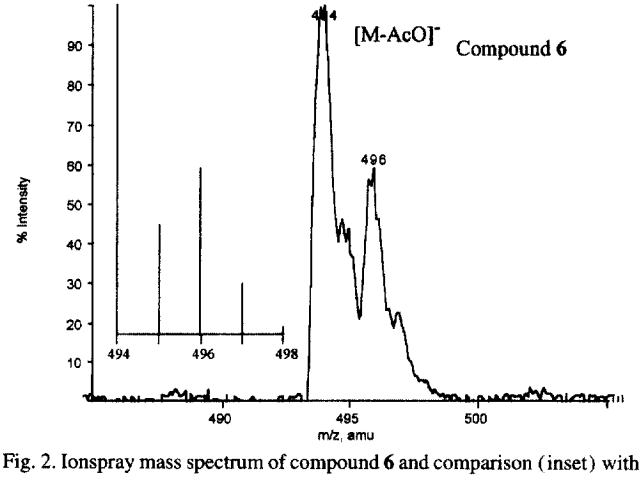



Fig. 2. Ionspray mass spectrum of compound **6** and comparison (inset) with the theoretical isotopic cluster.

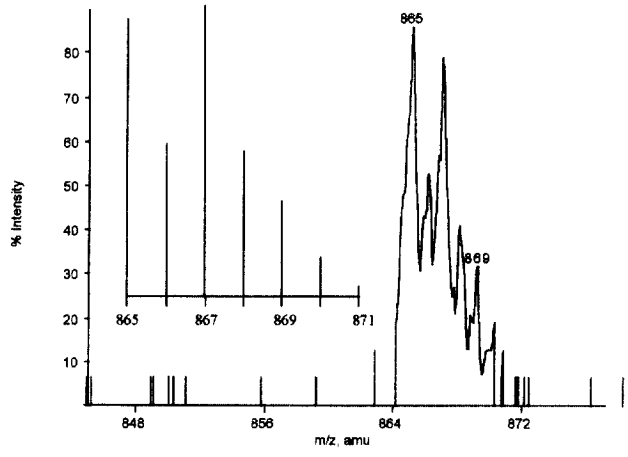



Fig. 3. Ionspray mass spectrum of compound **7** and comparison (inset) with the theoretical isotopic cluster.

two bridging oxygen atoms hold together two Cu-complex units. Indeed, we observed in this case an ion at *m/z* 865, corresponding to the protonated dimeric form, as confirmed by the comparison with the theoretical isotopic pattern (Fig. 3). In this case the MS analysis was determinant to identify this dimeric structure.

In the case of Cu complexed with a bidentate (O–N) ligand (**8**) we obtained a complex containing two ligand molecules per copper atom. The two bidentate ligands provide two negative charges, which neutralise the two positive charges of the Cu(II), and globally four coordinating atom donors, making a stable and fully coordinated complex. Of course, this complex is neutral and its ISI-MS spectrum shows an ion at *m/z* 924, corresponding to the protonated species.

The last case to discuss is the one of the dinuclear complex (**9**). In this case the complex contains two one-electron ligands (the two acetate groups) prone to be removed during the ionisation process. The ISI mass spectrum of this complex shows indeed two ions at *m/z* 733 and 338, attributable to the $[M-\text{acetate}]^+$ and to the doubly charged $[M-2\text{acetate}]^{2+}$ ions, respectively.

As far as the MS-MS fragmentation pattern is concerned, the high stability of the M–ligand bonds must be observed. Indeed, the fragmentation involves, at least at the beginning, loss of side chains from the ligand moiety, and only in some cases the ligand or part of it is removed from the complex. For instance, compound **1** fragments by loss of 2-vinylpyridine from one ligand moiety (M-105, *m/z* 812) and then the rest of the ligand is removed to leave the 1:1 complex (*m/z* 486). Compound **2** behaves more or less the same way. Compound **3** looks even more stable: we can observe the loss of a methyl group (M-15, *m/z* 524) probably from a t-butyl group of the ligand. Fragmentation proceeds then by loss of both methane (*m/z* 508) or isobutene (*m/z* 468). Fragmentation patterns of the other Mn complexes can be interpreted in the same fashion. As an example of a Cu complex, compound **9** fragments by loss of acetic acid (M-60, *m/z* 673) and the resulting ion is very stable (100% relative intensity) and there are only minor fragments due, for example, to the loss of pyridine. In no cases did we observe loss of one ligand as the first step of fragmentation.

## 4. Conclusions

Ionspray mass spectrometry revealed a very powerful technique for the characterisation of covalent organometallic complexes, provided that they can be ionised under ISI conditions in some way. In particular we found out that some complexes ionise by breakage of a polarised M–X bond, where X is an electron-withdrawing ligand, such as a chlorine or an acetate group. Some other complexes are present in solution in unexpected stoichiometric ratios, attributable to ionic complexes of the type $[(L_3)_2Mn]^+X^-$ in the case of manganese complexes with tridentate ligands or in a dimeric form such as in the case of the copper complex with O–N–O tridentate ligands. The structure of the complexes could anyway be rationalised in all cases. In conclusion, the ISI-MS approach can provide a very rapid characterisation even for complexes whose analysis is not trivial by the use of the most common spectrometric techniques, with the sensitivity and specificity typical of mass spectrometric methods.

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